

**Final Report (grant #NA06OAR4310049)**  
**Development of HCFCs as New Transient Tracers**

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**Total Request:**        1st Year: \$ 81,738   2nd Year: \$ 84,225   Total: \$ 165,963

**Project Objectives:**

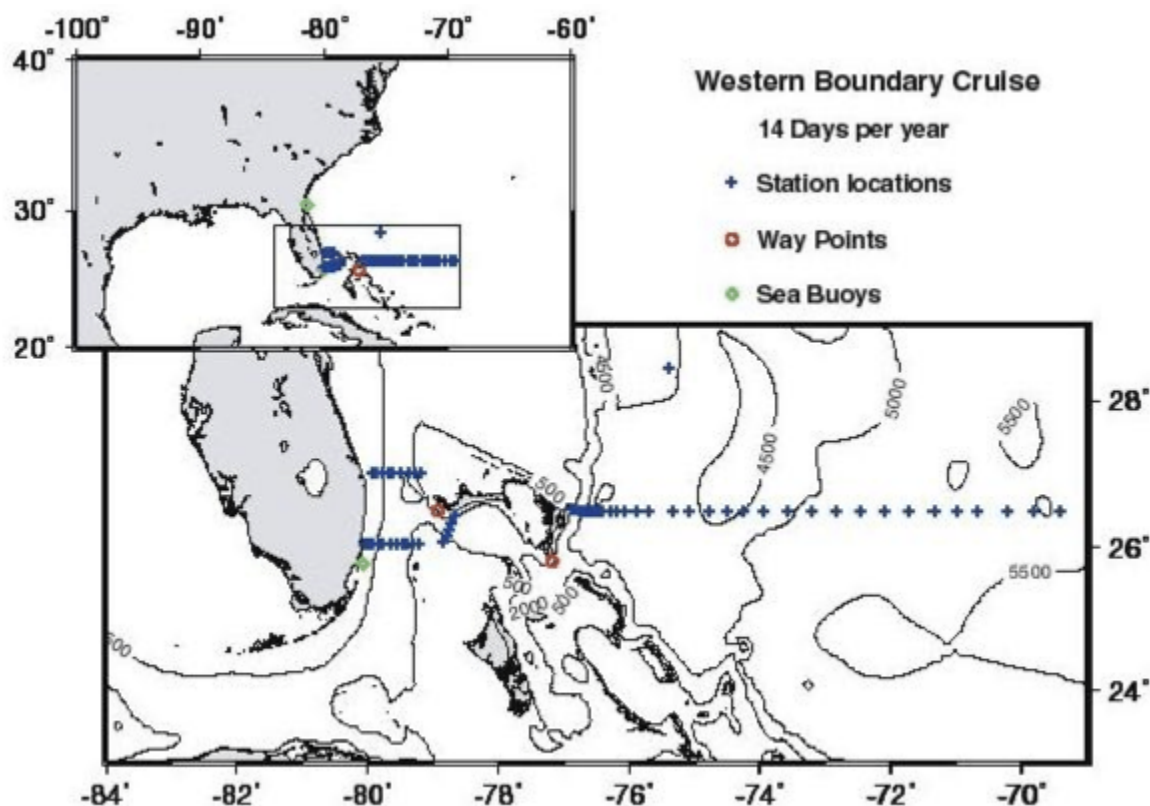
This project explores the use of CFC-replacement compounds (HCFCs and HFCs) as water mass tracers for young water masses in the Atlantic Ocean. The proposed new tracers are  $\text{CHClF}_2$  (HCFC-22),  $\text{CH}_3\text{CCl}_2\text{F}$  (HCFC-141b) and  $\text{CH}_3\text{CClF}_2$  (HCFC-142b), and  $\text{CH}_2\text{FCF}_3$  (HFC-134a). These compounds have been accumulating in the atmosphere since the late 1970s for HCFC-22 and the early 1990s for HCFC-141b, HCFC-142b and HFC-134a, and provide a mechanism for dating water masses which were in contact with the atmosphere since that time. CFC tracers (11, 12, 113) are no longer useful for dating recently ventilated waters, since their atmospheric levels have stabilized as a result of the Montreal Protocol.

The project consisted of: 1) shipboard measurements of depth profiles and surface saturation states of the HCFC tracers on two Atlantic cruises covering the area near Abaco, Bahamas where the Deep Western Boundary Current can be observed, and 2) assessment of the ability of these gases to be used as water mass age tracers. An additional cruise of opportunity was conducted. The measurements were made during the Gulf of Mexico East Coast Carbon Cruise (GOMECC) in July/August of 2007.

**Summary of Progress and Results:**

***WBTS Cruises***

Both of the specified Abaco, or Western Boundary Time Series (WBTS) cruises have been completed (Figure 1). This cruise is a repeat cruise conducted twice per year off of Abaco, Bahamas. For our study, these cruises were chosen to examine HCFC concentrations in Labrador Sea Water as it passes through the choke point off of Abaco, Bahamas. Given the fast transport of this water, we should see a distinct HCFC signal in these young waters.

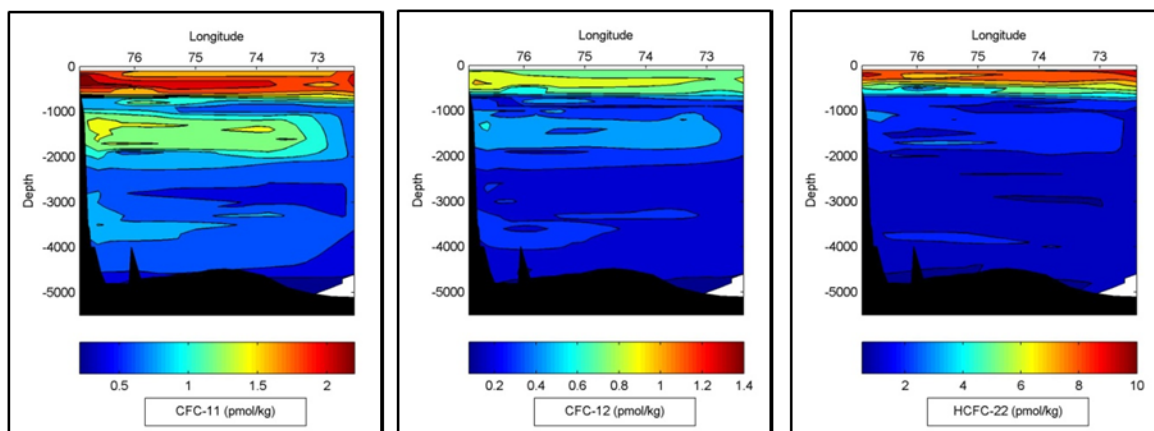


**Figure 1.** CTD stations occupied during the WBTS cruise.

During the first WBTS cruise, there were some serious instrument problems. Many of the discrete depth profile samples were compromised during analysis. Additionally, the early eluting compounds (CFC-12, HCFC-22, HCFC-142b, and  $\text{CH}_3\text{Cl}$ ) were lost for the surface saturation measurements. Typically we analyze samples for 21 chemical species (HCFC-22, CFC-12, HCFC-142b, Halon-1211, CFC-11, HCFC-141b, CFC-113,  $\text{CH}_3\text{CCl}_3$ ,  $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_4$  (PCE),  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHCl}_3$ ,  $\text{CHBr}_3$ ,  $\text{CH}_2\text{ONO}_2$ ,  $\text{C}_2\text{H}_4\text{ONO}_2$ , *i*- $\text{C}_3\text{H}_6\text{ONO}_2$ , *n*- $\text{C}_3\text{H}_6\text{ONO}_2$ ).

We tried to extract as much usable data as we could from the cruise. It is very difficult to get a picture of the water column from the sparse data. We corrected the problems with the depth profile instrument. They included both software and hardware problems. The software problem was the result of a bug in the Agilent Chemstation software that controls and collects the signal from the mass spectrometer. A patch for this problem became available in the summer after the first WBTS cruise, and we made the upgrade. Once the software was working properly, it was possible to diagnose and replace a contaminated solenoid valve.

The second WBTS cruise was quite successful and provided a much clearer picture of the core of the Deep Western Boundary Current as it passes through the Abaco choke point (Figure 2).



**Figure 2.** Preliminary data for sections of CFC-11(left), CFC-12(center), and HCFC-22 (right) located along 26.5N east of Abaco, Bahamas

These results are being included with the results of measurements of HCFC-22 made during the A16N cruise in 2003 in a paper discussing the distributions of HCFCs in the deep waters of the North Atlantic Ocean.

### **GOMECC Cruise**

We participated in a third cruise while working on this project. It is the Gulf of Mexico East Coast Carbon (GOMECC) cruise. Rik Wanninkhof (NOAA/AOML) was the PI for this cruise. We measured the same suite of halocarbons as before for both discrete depth profile samples and for continuous underway measurements of air and surface seawater. Please see the attached submitted manuscript for a discussion of this cruise and the results of the methyl bromide and methyl chloride measurements. Additional manuscripts are in preparation describing the HCFC/CFC results and the bromoform, dibromomethane and dibromochloromethane results from this cruise.

### **Conclusions**

The data we have collected suggest that HCFC-22 and HCFC-142b will be useful tracers of deep water formation and circulation. These gases persist in deep water and were observed in the “fast” Deep Western Boundary Current (Figure 2) [Yvon-Lewis, in prep.]. They appear conservative in surface waters as well and provide the same surface heating and cooling information as CFC-11 [Yvon-Lewis *et al.*, in prep.]. As the watermasses formed during the 90’s and early 2000’s continue to move through thermohaline circulation pathways, it will be very useful to include the HCFC measurements with the CFCs as a way of dating these water masses with greater temporal resolution.

## **Deliverables:**

Overall, we had 2 very successful cruises through this award. Four graduate students obtained valuable at-sea experience during these cruises. There were 4 presentations at national meetings and one at a PI meeting discussing data collected as part of this award. There is one *in press* publication, one submitted manuscript, and 3 *in prep.* manuscripts as a result of this award.

## **Posters**

Hu, L., S.A., Yvon-Lewis, Y. Liu, J.E. O'Hern, and J. Salisbury, Coastal emissions of methyl bromide and methyl chloride along the eastern Gulf of Mexico and east coast of the U.S., A43B-0298, *EOS Transactions Fall Meeting.*, 2008.

Liu, Y., S.A., Yvon-Lewis, L. Hu, J.E. O'Hern, and J. Salisbury, Bromoform and Dibromomethane in Coastal Waters During the Gulf of Mexico and East Coast Carbon (GOMECC) Cruise, A43B-0299, *EOS Transactions Fall Meeting.*, 2008.

Yvon-Lewis, S.A., L. Hu, Y. Liu, and J.E. O'Hern, Selected CFC and HCFC tracers observed during the Gulf of Mexico East Coast Carbon (GOMECC) Cruise, A53B-1321, *EOS Transactions Fall Meeting.*, 2008.

Yvon-Lewis, S A and J O'Hern, HCFCs and other Halocarbons in the Deep Western Boundary Current, ASLO/AGU/TOS/ERF, Ocean Sciences Meeting, Orlando 2-7 March 2008.

## **Papers**

Hu, L., S.A. Yvon-Lewis, Y. Liu, J. Salisbury and J.E. O'Hern (2009), Coastal emissions of methyl bromide and methyl chloride along the eastern Gulf of Mexico and east coast of the U.S., *Global Biogeochem. Cycles*, submitted.

Liu, Y., S.A. Yvon-Lewis, L. Hu, J. Salisbury and J.E. O'Hern, Bromoform, Dibromomethane and Dibromochloromethane in Coastal Waters During the Gulf of Mexico and East Coast Carbon (GOMECC) Cruise, *J. Geophys. Res.*, in prep.

Yvon-Lewis, S.A., E.S. Saltzman and S.A. Montzka (2009), Recent trends in atmospheric methyl bromide: analysis of post-Montreal Protocol variability, *Atmos. Chem. Phys.*, in press.

Yvon-Lewis, S.A., L. Hu, Y. Liu, and J.E. O'Hern, Selected CFC and HCFC tracers observed during the Gulf of Mexico East Coast Carbon (GOMECC) Cruise, A53B-1321, *J. Geophys. Res.*, in prep.

Yvon-Lewis, S.A., HCFCs in the deep waters of the North Atlantic Ocean, *J. Geophys. Res.*, in prep.